A mathematical theorem as basis for the second law: Thomson's formulation applied to equilibrium

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(February 1, 2008)

There are several formulations of the second law, and they may, in principle, have different domains of validity. Here a simple mathematical theorem is proven which serves as the most general basis for the second law, namely the Thomson formulation ('cyclic changes cost energy'), applied to equilibrium. This formulation of the second law is a property akin to particle conservation (normalization of the wavefunction). It has been stricktly proven for a canonical ensemble, and made plausible for a micro-canonical ensemble.

As the derivation does not assume time-inversion-invariance, it is applicable to situations where persistent current occur. This clear-cut derivation allows to revive the "no perpetuum mobile in equilibrium" formulation of the second law and to criticize some assumptions which are widespread in literature.

The result puts recent results devoted to foundations and limitations of the second law in proper perspective, and structurizes this relatively new field of research.

PACS: 03.65.Ta, 03.65.Yz, 05.30

I. INTRODUCTION

The second law is undoubtedly one the most known statements of statistical thermodynamics [1]. Its most known formulation is 'the entropy of a closed system cannot decrease'. Despite of its important role in the modern science — or may be even *due* to this role — its typical formulations are frequently folklore-minded and not very explicit. After all, what is precisely meant by entropy? Moreover, the law is rarely formulated rigorously [1]. This has led to a pertinent opinion that the second law is an empiric relation which is supported by observations, and at least not inconsistent with the formalism of quantum physics. This situation is especially unfortunate, since the absence of explicit formulations of the second law makes it difficult to study its generalizations or to limit its domain of applicability in extreme (quantum) conditions [2–6]. This became additionally complicated by the fact that the most typical formulations of the second law use the concept of entropy, which is a context-dependent quantity and which is frequently not observed directly. Indeed, the standard definition $dS = \text{d}Q/T$ is only an *identification* of the measured heat with a change in the *thermodynamic* entropy; 'measuring' entropy can be done in numerics if one determines the fraction of time that states are visited [7], but other definitions of entropy occur as well [8]. All by all this led to a disappointing situation, where far less known and less important subjects of statistical physics received much attention, while the second law itself still keeps its not very explicit and vague look. The situation became acute, when we discovered that several formulations of the second law (Clausius inequality, positivity of energy dispersion and entropy production) are violated in the standard model for quantum brownian motion, which is a harmonic quantum particle coupled to a bath of harmonic oscillators [4,6].

In the present paper we try to bridge this gap, and restate that the second law of thermodynamics — as formulated by Thomson — is just a rigorous theorem of quantum mechanics, comparable to particle conservation (normalization of the wavefunction). Standard quantum mechanics completely suffices for derivation of the theorem and its adequate interpretation. The Thomson formulation — and this is its main advantage over all other formulations — uses the unambiguous and well-defined concept of *work*. In contrast to entropy, work is a relatively straightforward quantity, and its use does not assume any particular caution. The proposed clear-cut Thomson formulation will allow us to establish a connection between the third and second laws, to analyze certain opinions expressed in literature about the second law, as well as to put into the proper perspective the recent attempts towards identification of limits of validity for the second law [4]. From the mathematical viewpoint the presented results are not completely new, since the main theorem appeared with a different, more complicated proof in works of Pusz and Woronowicz [9] and Lenard [10]. The purposes of these authors were quite different from ours, since they used the theorem as an argument towards describing the quantum equilibrium state through the Gibbs distribution.

For a general, pedagogic text on the history and today's status of thermodynamics and the second law, we refer to the recent work by Uffink [11]. For a collection and discussion of the original papers, see the book by Kestin [12]. A very recent discussion of the second law within the axiomatic thermodynamics was presented by Lieb and Yngvason [13]. A dialogue on the some of the definitions of entropy was reproduced by Maes and Lebowitz [8].

The setup of this paper is as follows. In section II we will derive the theorem for the quantum mechanical situation and in section III we consider the derivation for the classical case. In section IV we close with a discussion.

II. QUANTUM MECHANICAL PROOF OF THOMSON'S FORMULATION IN EQUILIBRIUM

Here we shall present a general proof of Thomson's formulation of the second law as applied to equilibrium: *No work can be extracted from a closed equilibrium system during a cyclic variation of a parameter by an external source.*

The idea of the following derivation was given by Lenard [10]. He was adopting to the physical language a more general proof given in [9]. This last proof is fairly difficult for the average physically-minded reader, since it uses the techniques of C^*-algebras. As a by-product of our present consideration we will significantly simplify the original derivation of Lenard.

A closed quantum statistical system is considered. The dynamics is described by the Hamiltonian $\mathcal{H}_0$. At the moment $t = 0$ an external time-dependent field is switched on, and the Hamiltonian becomes $\mathcal{H}(t)$. This field represents the influence of an external, deterministic source. The field is switched off at the moment t, and the Hamiltonian will be again $\mathcal{H}_0$. Thus we have a cyclic variation of a parameter with at least one period. Neither the explicit character of this parameter, nor the Hamiltonians $\mathcal{H}_0$ and $\mathcal{H}(t)$ have to be specified. It is only assumed that initially, before the variation has started, the system was in the equilibrium state described by the Gibbs distribution:

$$\rho(0) = \frac{e^{-\beta \mathcal{H}_0}}{Z}, \qquad Z = \text{tr } e^{-\beta \mathcal{H}_0}, \tag{1}$$

where $\beta = 1/T$ is the positive inverse temperature. In the time-interval t the source of the external field does work on the system. Since the system is closed before and after the variation, the work is equal to the difference between the final and initial energies:

$$W = \text{tr} \{ \mathcal{H}_0 \left[\rho(t) - \rho(0) \right] \}. \tag{2}$$

It can also be written alternatively as

$$W = \int_0^t \text{d}s \, \text{tr}[\rho(s) \frac{\text{d}\mathcal{H}(s)}{\text{d}s}], \tag{3}$$

where one uses integration by parts, and the equation of motion:

$$i\hbar \frac{\text{d}\rho(t)}{\text{d}t} = [\mathcal{H}(t), \rho(t)]. \tag{4}$$

Let us now go to the interaction representation and introduce a unitary operator V as

$$\rho(t) = e^{it\mathcal{H}_0/\hbar} \, V \, \rho(0) \, V^\dagger \, e^{-it\mathcal{H}_0/\hbar}. \tag{5}$$

Eq. (3) now reads

$$W = \text{tr}[\mathcal{H}_0 \, V \, \rho(0) \, V^\dagger] - \text{tr}[\mathcal{H}_0 \, \rho(0)]. \tag{6}$$

It is seen that as far as the work is concerned, any cyclic variation enters only through its corresponding unitary operator V. Our aim now is to show that W defined by (6) is nonnegative, or in other words, the final average energy is not smaller than the initial one. Notice especially that we compare only the average energies.

Due to Eq. (1) $\rho(0)$ and $\mathcal{H}_0$ commute, and thus have a common eigenbasis $|k\rangle$. Let us denote eigenvalues of $\rho(0)$ as $\{r_k\}$, and those of $\mathcal{H}_0$ as $\{h_k\}$. It holds that $r_k = \exp(-\beta h_k)/Z$. For simplicity we will consider a finite dimensional Hilbert space. One has

$$\text{tr}[\mathcal{H}_0 \, V \rho(0) \, V^\dagger] = \sum_{m,k=1}^n h_m v_{mk} r_k, \tag{7}$$

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where n is the dimension of the corresponding Hilbert space, and $v_{mk} = \langle m|V|k\rangle\langle k|V^\dagger|m\rangle$. Since V is unitary, $VV^\dagger = V^\dagger V = 1$, it follows that v_{mk} is double-stochastic:

$$v_{mk} \geq 0, \qquad \sum_{m=1}^{n} v_{mk} = \sum_{k=1}^{n} v_{mk} = 1. \tag{8}$$

One arranges the h_m in a non-decreasing order

$$h_1 \leq h_2 \leq \ldots \leq h_n, \tag{9}$$

which implies (due to the fact that the exponential function is monotonic) that the r_m are arranged as

$$r_1 \geq r_2 \geq \ldots \geq r_n \geq 0. \tag{10}$$

The work (6) reads in these variables

$$W = \sum_{m=1}^{n} h_m s_m - \sum_{m=1}^{n} h_m r_m \tag{11}$$

where s_m is defined as

$$s_m = \sum_{k=1}^{n} v_{mk} r_k. \tag{12}$$

Now we employ a summation by parts (the discrete analog of integration by parts)

$$\sum_{m=1}^{n} h_m s_m = -\sum_{m=1}^{n-1} (h_{m+1} - h_m) \sum_{i=1}^{m} s_i + h_n \sum_{k=1}^{n} s_k, \tag{13}$$

and the same with r_m replacing s_m, to obtain

$$W = \sum_{m=1}^{n-1} (h_{m+1} - h_m) \sum_{i=1}^{m} (r_i - s_i) + h_n \sum_{k=1}^{n} (s_k - r_k) = \sum_{m=1}^{n-1} (h_{m+1} - h_m) \sum_{i=1}^{m} (r_i - s_i) \tag{14}$$

In the second step Eq. (8) was used. To prove that $W \geq 0$, notice that $h_{m+1} - h_m \geq 0$. Therefore it suffices to show that

$$\sum_{i=1}^{m} r_i \geq \sum_{i=1}^{m} s_i, \tag{15}$$

Hereto one denotes $\phi_k^{(m)} = \sum_{j=1}^{m} v_{jk}$, which has the properties

$$0 \leq \phi_k^{(m)} \leq 1, \qquad \sum_{k=1}^{n} \phi_k^{(m)} = m, \tag{16}$$

as follows from (8). One then gets

$$\sum_{i=1}^{m} (r_i - s_i) = \sum_{i=1}^{m} r_i - \sum_{k=1}^{n} \phi_k^{(m)} r_k = \sum_{k=1}^{m} (1 - \phi_k^{(m)}) r_k - \sum_{k=m+1}^{n} \phi_k^{(m)} r_k \tag{17}$$

Now using the ordering (10) of the r_k, one gets the lower bound

$$\sum_{i=1}^{m} (r_i - s_i) \geq \sum_{k=1}^{m} (1 - \phi_k^{(m)}) r_m - \sum_{k=m+1}^{n} \phi_k^{(m)} r_m = \left(m - \sum_{k=1}^{n} \phi_k^{(m)} \right) r_m = 0, \tag{18}$$

where the last step follows because of Eq. (16). Therefore Eq. (15) has now been proven. Inserting this in Eq. (14) one finally has

$$W \geq 0 \tag{19}$$

This derivation concludes the proof of Thomson's formulation of the second law for this case: from a system in the equilibrium state work cannot be extracted in a cyclic process. The inequality sign says that work can nevertheless be done on the system, as is physically obvious.

At zero temperature the equilibrium state is the ground state. The inequality $W \geq 0$ is then obvious without any derivation, and confirms that no work can be extracted from the ground state.

III. MICROCANONICAL INITIAL DISTRIBUTION

The above analysis assumes that the initial state of the system is the Gibbs distribution. In the present section we shortly consider some other distributions of statistical physics. First let us notice that we only used two properties of the Gibbs distribution: commutation with the initial Hamiltonian and the opposite ordering of the corresponding eigenvalues, as given by Eqs. (9, 10). Thus, the no work-extraction principle: $W \geq 0$, is valid for all initial distributions which satisfy these properties. As a particular case, we mention the generalized microcanonical distribution or θ-distribution [14]

$$r_k = \frac{1}{m}\,\theta(m - k), \qquad 1 \leq k \leq n, \qquad 1 < m < n, \tag{20}$$

where $\theta(k)$ is step function: $\theta(x \geq 0) = 1$, $\theta(x < 0) = 0$. Thus all energy levels below a fixed level h_m are equally populated, while the energy levels larger than h_m are not populated. The monotonicity properties (9, 10) are obviously satisfied, so that $W \geq 0$ is also valid for the present case.

For the strictly micro-canonical ensemble one considers an energy shell $(\mathcal{E} - \mathrm{d}\mathcal{E}, \mathcal{E})$, which is a group of energy levels such that the difference $\mathrm{d}\mathcal{E}$ between the maximal and the minimal energy level of the shell is smaller than a characteristic uncertainty of energy [1]. Let the total number of levels within the shell be Ω. The states within the shell $\mathrm{d}\mathcal{E}$ are equally probable,

$$r_k = \frac{1}{\Omega} \tag{21}$$

for any level h_k belonging to the shell, while for other levels one has $r_k = 0$. It is seen that the arrangement of r_k's is non-monotonous as soon as the shell is located above the vacuum, i.e. if the minimal energy of the shell is higher than the vacuum energy. For this case a straightforward application of the above theorem is impossible. Let us see where precisely our proof fails. The simplest situation of this kind is a shell which consists of one single non-vacuum energy level. For simplicity suppose that we are trying to check Eq. (15) with a distribution $r_1 = 0$, $r_2 = r_3.... = r_n > 0$ (this is a shell with $n - 1$ levels, which just starts one level above the vacuum). As expected, Eq. (15) can be violated for $m = 1$

$$r_1 - s_1 = -\sum_{k=2}^{n} \phi_k^{(1)} r_k \leq 0. \tag{22}$$

More generally, a negative contribution to the work arises from systems that, due to the cyclic process, end up in energy levels below the shell. As a result, the theorem cannot hold in full generality, and may not apply, e.g., to small microcanonical systems.

The above arguments are simple enough to convince us that a proper formulation of the second law for the micro-canonical ensemble should be connected with certain limitations. As already discussed, one way is to require that the shell is so wide that it includes the vacuum state, and then one has the θ-distribution or generalized microcanonical distribution; the validity of $W \geq 0$ was shown above. Another way is to consider only those unitary operations which do not bring system to energies less than the lower shell-limit $\mathcal{E} - \mathrm{d}\mathcal{E}$; under this condition the theorem again applies, since the dangerous terms (those with energies below the shell) have vanishing matrix element v_{mk}. For large systems it is well known that almost all states are very near the maximal limit $\mathcal{E}$ of the shell. Let us suppose that for a macroscopic system with N degrees of freedom, $\mathcal{E}$ is proportional to N. The shell thickness $\mathrm{d}\mathcal{E}$ has to be much smaller than the typical uncertainty $\sqrt{N}$ of the energy. Let us choose $\mathrm{d}\mathcal{E} \sim N^\alpha$ with $\alpha < \frac{1}{2}$. Now given the fact that almost all systems of the ensemble have energy very close to the upper bound $\mathcal{E}$, extraction of energy less than N^α is ruled out for almost all members of the ensemble. On physical grounds one then expects that extraction of more energy is also very unlikely. This means that the central inequality $W \geq 0$ holds for all practical purposes in the micro-canonical ensemble.

IV. CLASSICAL PROOF OF THOMSON'S FORMULATION.

The above quantum result remains valid if the spectrum becomes dense, so the classical case is included into the consideration. Nevertheless, for the interested reader we will briefly outline the proof of the second law, when starting immediately from the classical formalism. Here the state of the system is described through the probability density

$\mathcal{P}(p,q,t)$ as a function of time t, the canonical momentum p, and the canonical coordinate q (in fact p and q can be arbitrary dimensional vectors; since the generalization to this case is obvious, it will not be discussed by us separately). The initial Hamiltonian and the time-dependent Hamiltonian are still denoted by $\mathcal{H}_0$ and $\mathcal{H}(t)$, respectively. The evolution of $\mathcal{P}$ is described by the Liouville equation:

$$\partial_t \mathcal{P}(t) = \mathcal{L}(t)\,\mathcal{P}(t), \qquad \mathcal{P}(t) = \mathcal{T}e^{\int_0^t ds\, \mathcal{L}(s)}\mathcal{P}(0), \tag{23}$$

$$\mathcal{L}(t) \equiv \frac{\partial \mathcal{H}(p,q;t)}{\partial q}\frac{\partial}{\partial p} - \frac{\partial \mathcal{H}(p,q;t)}{\partial p}\frac{\partial}{\partial q}, \qquad \mathcal{T}e^{\int_0^t ds\, \mathcal{L}(s)} \equiv 1 + \sum_{k=1}^{\infty} \int_0^t ds_1 \int_{s_1}^t ds_2 ... \int_{s_{k-1}}^t ds_k \mathcal{L}(s_k)...\mathcal{L}(s_1), \tag{24}$$

where $\mathcal{L}$ is the Liouville operator and $\mathcal{T}$ is the chronological symbol as defined above. For a cyclic variation the work in the classical situation reads:

$$W = \int dp\, dq\, \mathcal{H}_0(p,q)\left[\mathcal{P}(p,q,t) - \mathcal{P}(p,q,0)\right]. \tag{25}$$

Eq. (23) can also be written in the integral form:

$$\mathcal{P}(p,q,t) = \int dp'\, dq'\, \mathcal{P}(p',q',0)\,\mathcal{K}(p,q;t|p',q';0), \qquad \mathcal{K}(p,q;t|p',q';0) = \mathcal{T}e^{\int_0^t ds\, \mathcal{L}(s)}\delta(p-p')\,\delta(q-q'). \tag{26}$$

Now the work done by the external source reads:

$$W = \int dp\, dq\, dp'\, dq'\, \mathcal{H}_0(p,q)\,\mathcal{P}(p',q',0)\,\mathcal{K}(p,q;t|p',q';0) - \int dp\, dq\, \mathcal{H}_0(p,q)\,\mathcal{P}(p,q,0). \tag{27}$$

The analogy with Eqs. (6, 7) is by now fully obvious. In particular, the role of the discrete indexes i and k in those equations is now played by the continuous double-indices (p,q) and (p',q'); the role of v_{ik} is played by $\mathcal{K}(p,q;t|p',q';0)$. Due to its definition (26), $\mathcal{K}(p,q;t|p',q';0)$ does have the standard properties of the conditional probability distribution, and one additional property which makes it a double-stochastic (continuous) matrix:

$$\mathcal{K}(p,q;t|p',q';0) \geq 0, \qquad \int dp\, dq\, \mathcal{K}(p,q;t|p',q';0) = \int dp'\, dq'\, \mathcal{K}(p,q;t|p',q';0) = 1. \tag{28}$$

The only non-trivial property is the last one, but it quite clearly follows from (24, 26) upon noting that $\mathcal{L}$ is a differential operator and integrals similar to $\int dp'\, dq'\, \mathcal{L}(s_1)...\mathcal{L}(s_k)\delta(p-p')\,\delta(q-q')$ are equal to zero.

Once the property of the double-stochasticity and the essential similarity between (6, 7) and (27) is established, it is a matter of repetition to derive the proof of

$$W \geq 0 \tag{29}$$

in the classical case. The reader should notice that by saying this we ignore all convergence problems which can arise due to the continuous character of the considered classical situation. The most reasonable way to overcome such problems is to introduce an additional regularization. However, we will leave the situation as it is, since the readers who are sensitive to this kind of problems are just invited to get the classical situation as the limiting case of the above quantum proof (after all, the quantum formulation is the physical way to regularize the classical problem).

V. DISCUSSION

In classical physics there are many equivalent formulations of the second law. Examples are: non-decrease of entropy of a closed system, heat goes from high temperature to low temperature, the Clausius inequality $đQ \leq TdS$, non-negativity of the rate of entropy production and non-negativity of the rate of energy dispersion. A more folklore minded example is the absence of steady currents. In recent studies of quantum systems, several of these formulations have been questioned [2–4,6,5]. The fundamental question is then whether there is still a unique formulation that is satisfied in all cases. The aim of this paper is to demonstrate that there indeed exists such a formulation, and it is related with work, which, fortunately, is more accessible than heat and certainly more accessible than entropy, for which there are many definitions [8].

In the present section we will discuss the above theorem and its relations with the standard understanding of the second law, as well as we outline some relatively straightforward applications of the above theorem.

It is clear that the theorem forbids even one single work extraction cycle. This is to be put in contrast with the following known version of the second law: No *perpetuum mobile of the second kind* (i.e., a device which makes as many work-extracting cycles as one pleases) exists. It is a particular case of our theorem, but we now point out that it is in fact much more weaker, as its validity depends only on the *existence* of a ground state. This ground state does not have even have to be unique, as required for the validity of the third law [1]. Indeed, starting from *any* state and making sufficiently many work-extracting cycles with a finite extracted work per cycle, one will decrease the final average energy of the system below its ground state energy, which is impossible. So already a clear-cut formulation of the statement allows us to unmask the above *no perpetuum mobile* statement as a basically trivial consequence of quantum mechanics, rather than a deep theorem on (quantum) statistical physics. Our new theorem (even one cycle is forbidden) heals the problem, by forbidding 'perpetuum mobile' with any finite number of cycles, at least as long as one starts in equilibrium.

When proving the above theorem we did not use any special property of the initial Gibbs distribution, except for its commutation with the initial Hamiltonian and the opposite ordering of the corresponding eigenvalues (see Eqs. (9) and (10)). If the initial distribution is Gibbsian but the temperature is negative, this ordering property is lost, and the theorem does not hold. This explains the role played by negative temperature for lasers and masers [15], where positive work extraction is the main state of affairs. However, for other initial distributions that do satisfy these properties, the derivation applies as well. The most interesting case is the generalized micro-canonical ensemble or θ-ensemble, where all states below a given energy are equally probable. In typical situations a vast majority of the states have energy very close to the maximal energy, implying that, at least in statics, this generalized ensemble is equivalent to the micro-canonical ensemble itself. The same property puts forward that also our theorem applies for all practical purposes to the micro-canonical ensemble.

Yet another line of generalization arises when one is noting that the features of the Hamiltonian $\mathcal{H}_0$ under time-inversion were irrelevant for the proof. Thus, the studied system may well contain an external magnetic field. In such a situation the system can contain persistent currents in the equilibrium state. Examples are Landau diamagnetism [1], vortices in conventional superconductors [16], that may last days, boundary currents in the quantum Hall effect and persistent currents in mesoscopic rings. These effects are pretty counterintuitive from the classical thermodynamical viewpoint, and at the first glance may even appear as a violation of the second law. In particular, one of the widespread folkore-minded formulations of the second law refers to the impossibility of ongoing motion in the equilibrium state, and the persistent currents give an example of such a motion. Nevertheless, it does not imply any contradiction with the second law in the Thomson formulation, and also shows that for the present case the time-inversion invariance does not have any direct connection with the second law. Notice in this context that the second law in the equilibrium Thomson formulation was proven under the condition of time-inversion-invariance (see [18,19] and refs. therein). Since the invariance property is rather strong, the authors of these works got somewhat more detailed results than just the non-negativity of the work $W \geq 0$. Whether these results are valid for the considered more general case is still an open problem.

We like to stress that our theorem also applies when the total closed system consists of a subsystem and a heat bath, that interact with each other. In that situation the typical case is that a work cycle is made by manipulating a parameter of the subsytem. This is the situation considered in Ref. [6], and it could be checked that, when starting from equilibrium, the total work for making a cyclic change is always positive.

Let us notice that, after one cycle has been made, the system can locally return to equilibrium. Then surplus of energy runs away (dissipates) in the bath. When this process has settled, additional cycles cost additional work. Employing a standard argument, we can now show that non-cyclic changes, that are made in such a manner that afterwards one waits long enough to erase memory effects, also disperse energy. Indeed, by closing the cycle, there should always be dispersion, and this is only possible in all cases if each part disperses energy.

Finally, we would like to analyze two widespread opinions about the second law. In their book [1] Landau and Lifshitz state that the second law is incompatible with the microscopically reversible quantum dynamics, and that the second law can somehow be connected with the quantum measurement process, which in view of these authors is an inherently irreversible process imposed on the reversible quantum formalism. As we see above, no quantum measurement process is directly involved into the derivation of the second law, and the standard quantum-mechanical formalism is completely enough. Moreover, the dynamics of the system is unitary, i.e. it is invertible as precisely as one wishes, so that no arrow of time is involved in the presented derivation of the second law.

Within another school of thinking, Zurek and his coworker [17] claim that the second law does arise as a consequence of the interaction between a quantum system and its *thermal* environment (environment-induced superselection rules). This is again not supported by the above proof, since it does not suppose the existence of a thermal environment,

although such a case is not excluded, provided that the system and its environment are considered within one closed system. Of course, this remark does not mean that the second law has nothing to do with thermal environments in general. They are just not necessary for the rigorous statement of the Thomson formulation applied to the equilibrium state of a closed system.

In conclusion, we have analyzed a mathematical theorem which serves as a basis for the derivation of the second law in the Thomson formulation. Once this clear-cut derivation is given, it is a matter of a simple logic to rule out some pertinent pre-supposes on the second law. In particular, we analyzed the "no perpetuum mobile" principle, which within the quantum theory was seen to be almost a trivial statement akin (and even weaker) to the third law. It is hoped that the present paper will put into the proper perspective the research devoted to the microscopical foundations and limitations of the second law [2–6], since it is absolutely necessary to have a rigorous formulation of this law within the quantum statistical thermodynamics before consideration of its limits and its generalizations. From our viewpoint, neither the folklore-minded statements typically encountered in textbooks, nor rigorous derivations within the axiomatic (formal) thermodynamics fully meet this goal.

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